UNITED STATES PATENT APPLICATION

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FOR

CYLINDRICAL TUBE FOR INDUSTRIAL CHEMICAL INSTALLATIONS

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CYLINDRICAL TUBE FOR INDUSTRIAL CHEMICAL INSTALLATIONS

FIELD OF THE INVENTION

The invention relates to a tube to be used in a device for heating of a gas or liquid medium that is transmitted from one end of said tube to the other end thereof while simultaneously being heated such that a chemical reaction occurs. The heating can occur for instance by heating the exterior tube wall or by providing heating directly through the walls.

BACKGROUND OF THE INVENTION

In the description of the background of the present invention that follows reference is made to certain structures and methods, however, such references should not necessarily be construed as an admission that these structures and methods qualify as prior art under the applicable statutory provisions. Applicants reserve the right to demonstrate that any of the referenced subject matter does not constitute prior art with regard to the present invention.

In order to obtain an acceptable yield of a product, such as ethylene in an ethylene cracker, it is necessary to use a tube that is free from cracks on its inner side. The tube must also be resistant towards exposure of those products that are formed inside such tube. When using materials currently for such tube applications it frequently occurs that oxides are being formed on the inside of such tubes and that easily come apart therefrom, which reduces the lifetime of such tubes. At the same time there is a problem with carbonizing since a deposit of a carbon compound is formed on the inside of such tube. The larger deposit that is formed, the smaller is the amount of gas that can be passed through such tube. At the same time the heat transformation will decrease which results in an impaired economy.

Known furnaces for the cracking of hydrocarbon are usually provided with cast tubing of nickel-based alloys with high amounts of chromium. This leads to some disadvan-tages because such tube materials are more expensive and further, high nickel content can be a catalyst for undesirable coking.

Also, the ability of tubes made from such materials to maintain their original shape, which normally are characterized as high temperature materials, is not satisfactory in certain applications.

In a cracker, a decomposition of a hydrocarbon occurs. The starting materials could be for instance naphta or propane mixed with water vapor. When the material passes through the tubes in the cracking furnace the temperature is increased to above 800° C. Important products that are being obtained are for instance ethylene and propylene. Also hydrogen gas, methane, butane and other hydrocarbons are being formed. In order to avoid undesired reactions it is essential that such heating occurs very rapidly and that the obtained products are subjected to quenching - the residence time in the furnace only amounts to some tenths of seconds. The temperature in the furnace can reach 1100-1200° C -and the tube material temperature in the furnace could be above 1100° C. The heating of the furnace room could be obtained by combustion of gases from the cracking process such as hydrogen and methane, and a furnace can be equipped with a large number of gas burners that can be arranged in the floor or in the walls such furnace.

The tubes that are used in the furnace shall have good shape permanence to heat and shall be able to withstand high temperatures. They must also be resistant towards oxidation and corrosion so as to withstand the atmosphere in the furnace room. The carbon potential inside the tubes in the furnace is very high and the tube material should therefor be able to withstand carburization and carbide formation. Minor amounts of sulphur are often being added to the starting material and therefor the tubes must also have good resistance towards sulphur and sulphur compounds.

SUMMARY OF THE INVENTION

The present invention relates to a new type of finned tube to be made of a material that improves resistance towards the environment in furnaces for the cracking of hydrocarbon external to the tube, as well as the particular environmental conditions occurring inside the tube.

According to one aspect, the present invention provides a metal tube for use in furnaces where gas and liquid formed media is being pressed through such tube from its inlet end to its opposite end while being subjected to substantial heating and decomposition therefrom, the metal tube comprising: a body; a smooth outer surface; and an inner surface with a profile; wherein the body is made of a stainless iron-nickel-chromium base alloy comprising, in weight-%: -max 0.08% C, 23-27% Cr, 33-37% Ni, 1.3-1.8% Mn, 1.2-2% Si, 0.08-0.25% N, 0.01-0.15% rare earth metals, and normal impurities; and the profile comprises a plurality of valleys or recesses, said valleys or recesses extending longitudinally along the tube, and having a smoothly curved bottom.

By forming a tube with a high strength stainless steel with good resistance towards oxide flaking and carbonizing, the chemical resistance, and the economy of such tubing and furnaces have been improved in a special way. This has brought about a tube having very good heat transfer properties combined with substantially improved resistance toward too quickly appearing carbonizing, carburization and oxide flaking due to the products produced during such transfer of materials within the tube.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

The objects and advantages of the invention will become apparent from the following detailed description of preferred embodiments thereof in connection with the accompanying drawings in which like numerals designate like elements and in which:

Fig. 1 shows a tube with a formation in accordance with the invention.

Fig. 2 shows a cross section of the tube of Fig. 1.

Fig. 3 shows the weight change during oxidation in air and 1000° C as a function of the exposure time of said tubes.

Fig. 4 shows schematically how the carburizing profile was measured on rod shaped specimen for analyzing the carbide content.

Fig. 5 shows the measurement results for carburizing in terms of area function of carbides.

DETAILED DESCRIPTION OF THE INVENTION

In Fig. 1, a tube 10 is designated having an entry end portion through which a gas formed medium such as hydrocarbon and steam shall be urged towards the exit end portion while undergoing a chemical reaction.

In the embodiment as shown, the inner surface 11 of the tube 10 is provided with re-cesses 13 and ridges 14 of a sinusoidal shaped contour, while the outer surface 16 is substantially smooth or arcuate, see Fig. 2. The ridges 14 and the recesses 13 are provided with a rounded profile to avoid fatigue cracks.

In accordance with an alternative embodiment, the interiorly provided recesses 13 of the cylinder 10 can be helically provided in the longitudinal direction of said tube.

Alternatively, instead of being cylindrical in its entire length, said tube can be conically shaped from its inlet end to its outlet end.

It has been found that the shape permanence during heating of tubes according to the present invention can be improved if the tubes are made by pilger rolling over a mandrel in principle in the manner as shown and described in U.S. Patent No. 4,095,447. Alternatively, however, such tubes could be made in the manner described in U.S. Patent No. 5,016,460. Instead of pilger rolling over a mandrel drawing over a mandrel can be applicable.

The steel material to be selected for such cylinder 10 is a stainless iron-nickel-chromium base alloy with an austenitic structure and otherwise strictly controlled and optimized amounts of alloy constituents. The alloy contains, in weight-%, max 0.08% C, 23-27% Cr, 33-37% Ni, 1.3-1.8% Mn, 1.2-2% Si, 0.08-0.25% N, 0.01-0.15% rare earth metals and Fe and normal impurities. The amount of rare earth metals are preferably 0.03-0.10% which promotes the formation of a thin elastic adherent oxide film when the material is exposed to oxidizing environment at high temperatures. The amount of nitrogen should preferably be 0.13-0.18%, and the amount of silicon should preferably be 1.3-1.8%.

By the above given choice of material, it is possible to achieve unexpectedly superior, substantially longer, usage time periods without interruption for exchanging tubes while simultaneously also achieving a substantially smaller amount of deposits of carbon compounds on the inner tube side, which furthermore improves the usage economy since smaller amounts of deposits on the tubes enables larger amount of hydrocarbon and steam to be transported through the tubes, for instance in connection with the manu-facture of ethylene.

A further improvement can be achieved by providing a chromium oxide layer on the inner tube surfaces which will prevent the diffusion of carbon into the material by oxidation of said tubes before they are put into usage.

Fig. 3 illustrates the results of a study of the tendency toward oxide flaking in tubes made of Sanicro 39 type material according to the invention put in relation to some conventional materials that are being used in corresponding applications. For reference purposes this study included both forged and cast alloys which are well established materials for cracker tubes in ethylene furnaces, for instance a material marketed by International Nickel Inc. under the designation INCO 803, one material marketed by Sumitomo Metals Ltd under designation HK4M and a cast alloy with designation HP45-Nb. The analysis of the various reference materials is given in the table below.

Alloy	Cr	Ni	Si	Mn	C	N	Nb	Ti	Al	
HP45-Nb	23.6	36.9	1.4	1.22	0.17	0.046	1.2	--	--	
Inco 803	25.8	35.3	0.65	0.90	0.075	0.013	--	0.55	0.52	
HK4M	25.3	24.5	0.41	1.12	0.21	0.017	--	0.46	0.33	
Sanicro39	24.9	34.8	1.5	1.4	0.048	0.166	--	--	--	REM=0.05

The diagram in Fig. 3 shows the weight change during oxidation in air at 1000°C as a function of the exposure time for the tubes.

As appears from the diagram in Fig. 3 the obtained result shows that the oxides being formed more easily come apart from these reference materials when compared with the material Sanicro 39 selected according to the invention.

The carburizing tests were carried out so as to be similar to the ethylene environment present in the aforementioned cracker applications by providing shifting carburizing and oxidizing environments. The carburizing occurred in a gas mixture comprising carbon monoxide, hydrogen gas and methane in a mixture which was at a temperature of 1050° C and gave an oxygen potential corresponding to 10-15 atm and a carbon activity > 1. After being exposed for 120 hours to this carbonizing environment the coke that had been formed was taken out by introducing air to combust the coke. The time period for the carburizing/oxidizing cycle varied between 135-140 hours. The total testing time was 1104 hours corresponding with 8 cycles as set forth above. The temperature was kept constant at 1050° C during the entire first test. The geometry of the test rods was 8 mm x 8 mm x 20 mm.

After the test was completed the test rods were taken out and a cross section thereof was studied by looking upon how the area fraction of carbides varied along a selected line. The cross section of said test rods had a square shaped outer surface and with this test rod design it was found that the carbonizing was much depending on where on this outer surface the measurement was made. Areas close to corners and edges appeared to be more sensitive to carbonizing than those surfaces that were planar. In Fig. 4, it is shown the position of the lines that are analyzed in the cross section of the test rod. The first line (Prof 10) was located 0.8 mm (10% of the edge length) into the material along the outer surface. The second line (Prof 50) was located 4 mm from a corner whilst being extended through the center of the test rod. In Fig. 4 it is schematically shown how carburizing varies depending on whether the location is close to an edge or extending far into a planar surface.

This figure also schematically shows how the carburizing depth varies depending on the distance from a corner. The grey marked area represents the carburized area and the white field represents the noncarburized area. It should be noted that the carbonizing depth is larger in the corners of the test rod.

In Fig. 5 the results from the area fraction analysis of carbides are presented. The x-axis represents the distance from the start point at one outer surface (0-8 mm) and the y-axis shows the measured area fraction of carbides (%). The diagram shows that Sanicro 39 and HP45-Nb are not affected by carburizing from planar surfaces (Prof 50) and out of these two Sanicro 39 appeared with the best resistance towards carburizing in the area close to the corners or the edges (prof 10). The alloy 803 was affected by massive carburizing in the comer areas and also appeared with strong carburizing on the planar surfaces. The alloy HK4M was subjected to carburizing to its maximum through the entire material.

While the present invention has been described by reference to the above-mentioned embodiments, certain modifications and variations will be evident to those of ordinary skill in the art. Therefore, the present invention is limited only by the scope and spirit of the appended claims.